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ANALYSIS OF NITROGEN TRIFLUORIDE

Final-Interim Report

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APRIL 1976

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A gas chromatograph technique for the analysis of NF_3 is described wherein $N_2(O_2)$, CO, NO, CF_4, NF_3, CO_2, N_2O, SF_6 and possibly N_2F_2 are separated isothermally on a single column. In addition, a simple total reactive fluoride measurement is presented.

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INTRODUCTION

Interest in the use of nitrogentrifluoride (NF_3) as a fluorine oxidizer has recently dictated the need for a military propellant specification. Since the specification represents the portion of a procurement contract which defines the quality of the product, it is necessary that the quality tests be reliable and, at the same time, as simple as possible so that a high quality product is assured without unnecessarily high analytical costs.

NF_3 is a relatively inert compound at ambient temperature, however, the possible impurities can vary from highly reactive (e.g. HF, F_2, N_2F_4, COF_2, N_2F_2) to very inert (e.g., N_2, O_2, CF_4, CO_2, N_2O). Also impurities of intermediate reactivity (e.g., NO, NO_2, CO) can be present.

Analysis of such a potentially complex mixture requires some compromise with respect to specificity in order to maintain reasonable analysis costs. A brief inspection of the objectives for the analysis of the propellant reveals that the impurities can be grouped into several categories; (a) those that lower performance by dilution, (b) those that lower performance by interference with the fuel/oxidizer reaction, and (c) those that affect the storability of the propellant. A number of these potential impurities are categorized in Table I.

Table I, Impurities Categorized by Detrimental Effect

a (diluent)	b (interference)	c (corrosive)
N_2	O_2	HF
CF_4	CO	F_2
SF_6?	NO	N_2F_2
	CO_2	N_2F_4
	N_2O	COF_2
	HF	
	COF_2	
	NO_2	

Group (c) can be determined without specificity since the common active atom is fluorine. A total active fluoride determination will provide a greater penalty for N_2F_4 contamination than for HF on a mole basis. This imbalance is justified since corrosion potential should be proportional to active fluoride concentration. Total oxidizing capacity of NF_3 impurities has been measured with aqueous I^-(1) and solid Cl^-(2); however, in both cases HF was determined separately.

The following describes a less complicated test method for NF_3 using only gas chromatography and a total active fluoride measurement.

EXPERIMENTAL

Gas transfer manifold. The manifold shown in Figure 1 was fabricated from Hoke type 415 "tee" pattern and Hoke type 413 "straight" pattern valves. The differential pressure gauges are 0 - 760 mm and 0 - 20 mm Wallace and Tiernan types FA 145 and FA 111, respectively. Each component was cleaned with trichlorotrifluoroethylene prior to assembly and the assembled manifold was passivated with HF overnight. All gas mixtures were prepared using this apparatus.

I. R. cell. The I. R. cell used was a 100 mm pathlength micro gas cell equipped with BaF_2 windows (Barnes Engineering, 906-0029) and packless valves (Hoke, 4552Q4M). The cell was also cleaned, followed by passivation with HF.

Total active fluoride. The sample reservoir was assembled from a 280 cu. in. aviator's breathing oxygen tank, Hoke type 413 valves, and a 0 - 760 mm absolute pressure gauge (Matheson, 63 - 5601). The bubbler was fabricated from a Fisher-Porter 100 ml aerosol compatibility tube, a "drilled" Swagelok tee, and 1/4 in. O.D. polyethylene tubing which was heat-sealed at one end and re-opened by drilling several 0.005 in. holes into the heat-sealed area. For increased safety, polytetrafluoroethylene tubing, plugged and drilled, would probably have been a better choice. The bubbler containing 40 ml of 0.1N-NaOH and the sample reservoir are pictured in Figure 2. The apparatus is shown in the configuration used for sampling NF_3. When HF mixtures were

Figure 1, GAS TRANSFER MANIFOLD

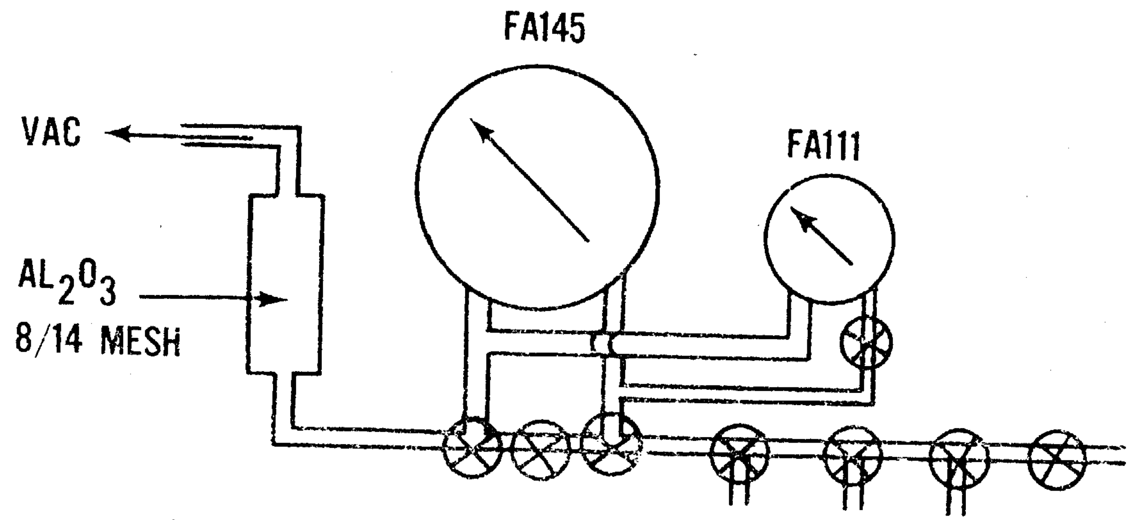
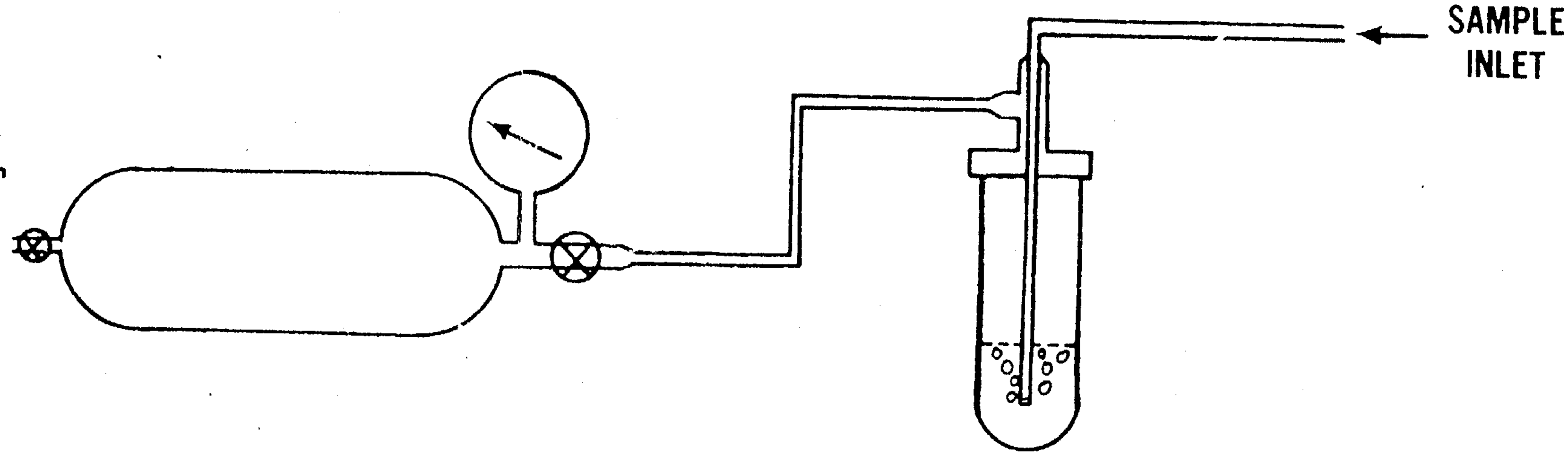


Figure 2, TOTAL ACTIVE FLUORIDE APPARATAS.



tested, they were prepared in the sample reservoir and drawn through the bubbler, appropriately connected, using a water aspirator. In both cases sample size was computed from the reservoir volume and the pressure change indicated by the gauge. After absorbtion of the sample, the 0.1N-NaOH was transferred to a vessel containing an equal volume of Orion TISAB solution and the fluoride ion concentration was measured using an Orion Fluoride Selective Ion electrode, a Ag/AgCl reference electrode, and an Orion Model 801 Digital pH/MV meter.

Infrared Spectrophotometer. Infrared spectra were obtained using the gas cell described and a Beckman Model 4240 Infrared Spectrophotometer equipped with scale expansion.

Gas Chromatograph. The chromatograms were obtained with a Hewlett-Packard Model 5830A gas chromatograph equipped with a gas sampling valve, a thermal conductivity detector, and a 20 ft. by 1/8 in. O. D. stainless steel column packed with 80/100 mesh Chromosorb 102 (Johns-Manville). An active fluoride scrubber was inserted between the sample source and the gas valve. The Scrubber consisted of an 8 in. by 1/4 in. O. D. glass tube packed with 4 in. of 40/50 mesh KI followed by 4 in. of 40/50 mesh $Na_2S_2O_3 \cdot 5H_2O$. The outlet line of the gas valve was located over a propane/air burner to destroy the excess NF_3 which was passed through the valve. NF_3 was analyzed both with and without the active fluoride scrubber in place. Test conditions for the gas chromatograph are listed in Table II.

Table II, Gas Chromatograph Test Conditions

Detector type	thermal conductivity
Helium flow ml/min.	15
Sample Volume ml	1 @ ambient pressure
Column temp. ^{o}C.	35
Inlet temp. ^{o}C.	85
Detector temp. ^{o}C.	125

Calibration standards. All gas mixtures were prepared directly by partial pressure measurement; no serial dilution was used. Trace contaminants were 99.0% pure or better and diluents were greater than 99.99% pure helium or nitrogen.

RESULTS AND DISCUSSION

Infrared analysis. Figures 3 and 4 are infrared spectra of the calibration gas mixture described in Table III and a sample of NF_3, respectively. Both were obtained at 760 mm using the same cell. Data from Pierson, et al (4) and Simons (5) aided in band assignment. Inspection of the figures shows that absorption regions for many of the anticipated contaminants are not located in windows of the NF_3 spectrum. In addition, poor sensitivity, at the test conditions used, will likely allow only CO_2, CF_4, and N_2O to be determined without scale expansion. Although not illustrated by the figures, the useful absorbtion band for N_2F_4, 1270 cm^{-1}(3), is likely overlapped by the CF_4 band.

Gas chromatograph analysis. A calibration standard containing a variety of compounds anticipated as impurities in NF_3 was prepared and analyzed using the test conditions described. Table III shows the composition of the mixture and the sensitivities of each component.

Figure 3, TRACE GAS MIXTURE/HELIUM MATRIX (760mm)

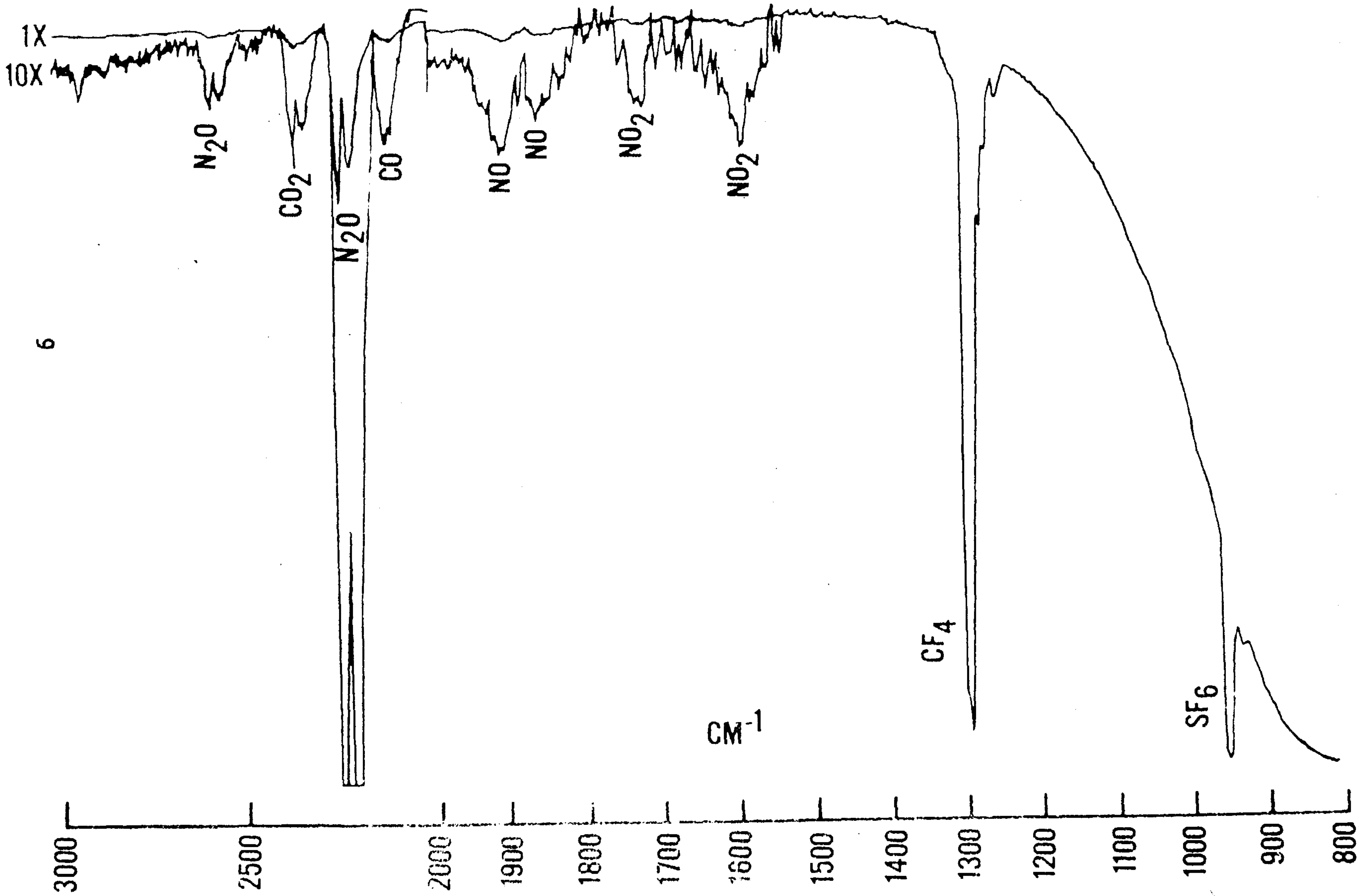


Figure 4, NF_3 (760mm)

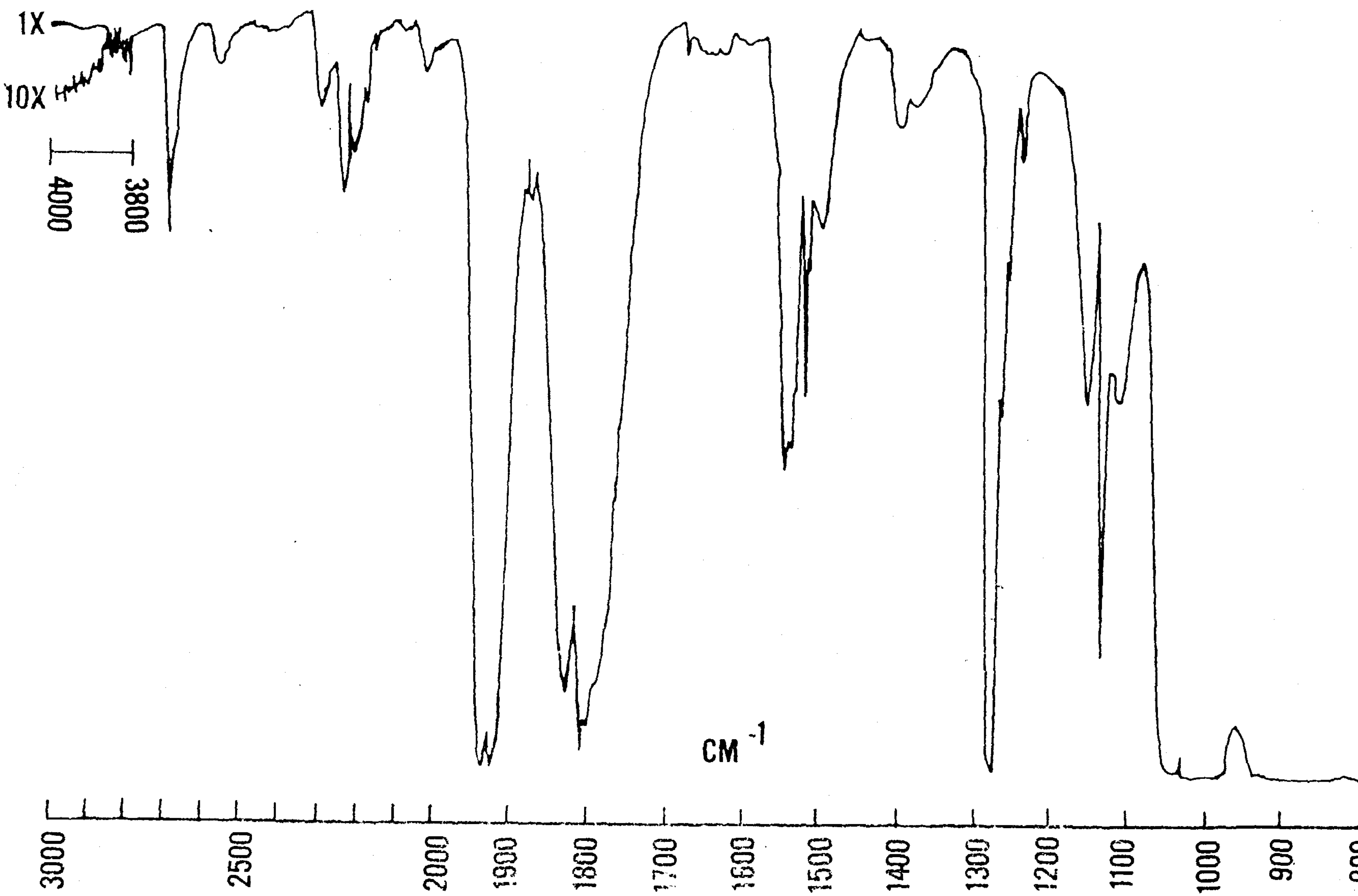


Table III, Calibration Standard Analysis Results

Component	Concentration (ppm/vol)	Sensitivity (ppm/area unit)
$N_2(O_2)$	920	0.0710
CO	1010	0.0774
NO	920	0.0868
CF_4	920	0.0546
CO_2	520	0.0597
N_2O	920	0.0644
SF_6	920	0.0466

Figure 5 is a typical chromatogram of the calibration mixture, and Figure 6 is a chromatogram of an NF_3 sample using the same test conditions. Adequate resolution is illustrated for each component in the mixture. _Cis_ and _trans_ N_2F_2 have been reported to appear between the NF_3 and CO_2 peaks (2). Unfortunately, oxygen and nitrogen are not resolved with this column, however, the air peak can be diverted with a column switching valve to a Molecular Sieve column if oxygen/nitrogen separation is desired.

Since some of the potential contaminants in NF_3 are strong oxidizers and very corrosive, some means of removing these compounds was desired so that the chromatograph would not be damaged. The $KI/Na_2S_2O_3$ scrubber was installed and the data shown in Table IV was acquired to determine if the scrubber affected the NF_3 analysis results.

FIGURE 5, GAS CHROMATOGRAM OF CALIBRATION GAS MIXTURE

LEGEND:

TIME	COMPONENT
3.84	$N_2(O_2)$
4.09	CO
4.31	NO
5.16	CF_4
11.58	CO_2
15.33	N_2O
16.65	SF_6

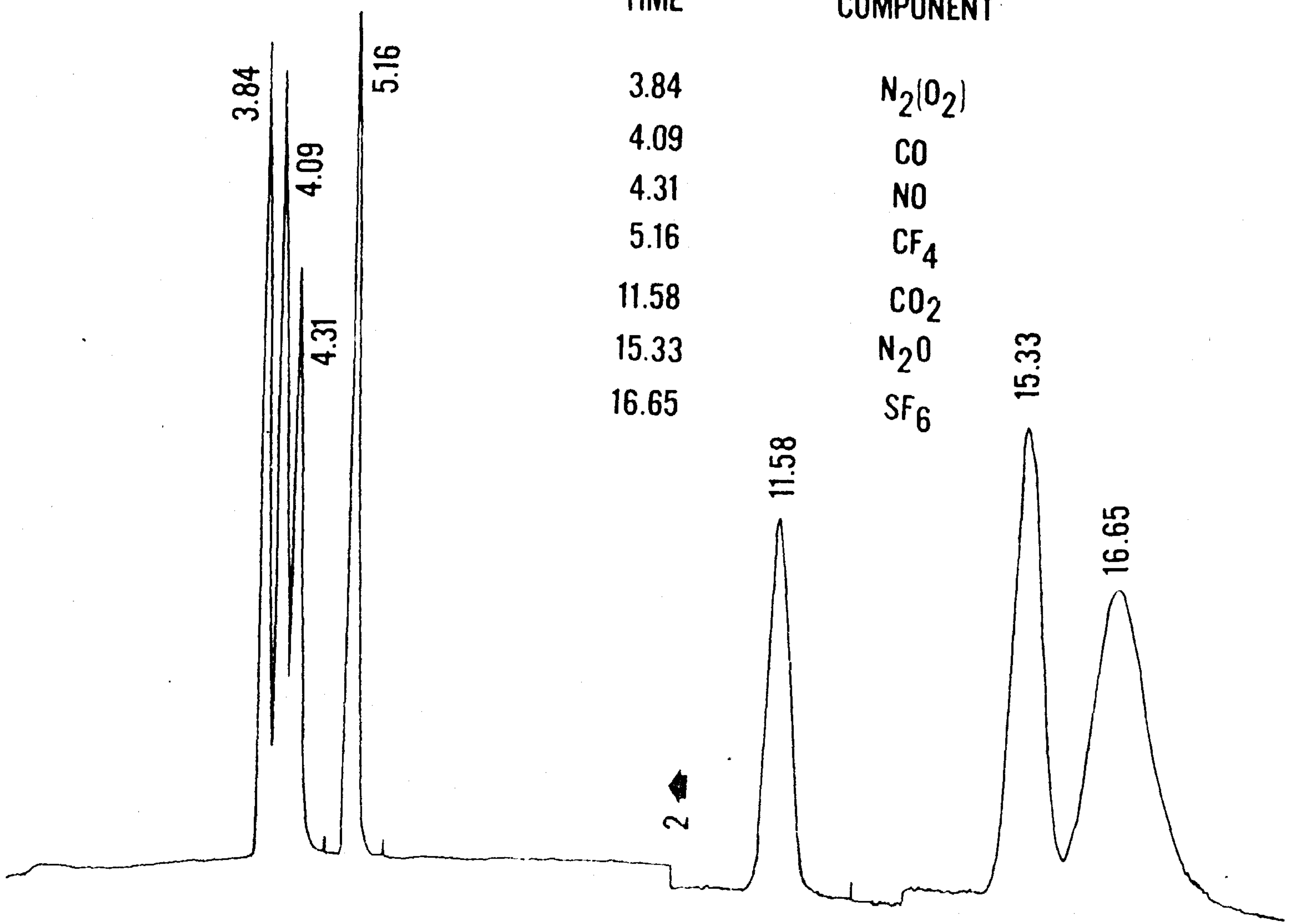


Figure 6, GAS CHROMATOGRAM OF NF_3

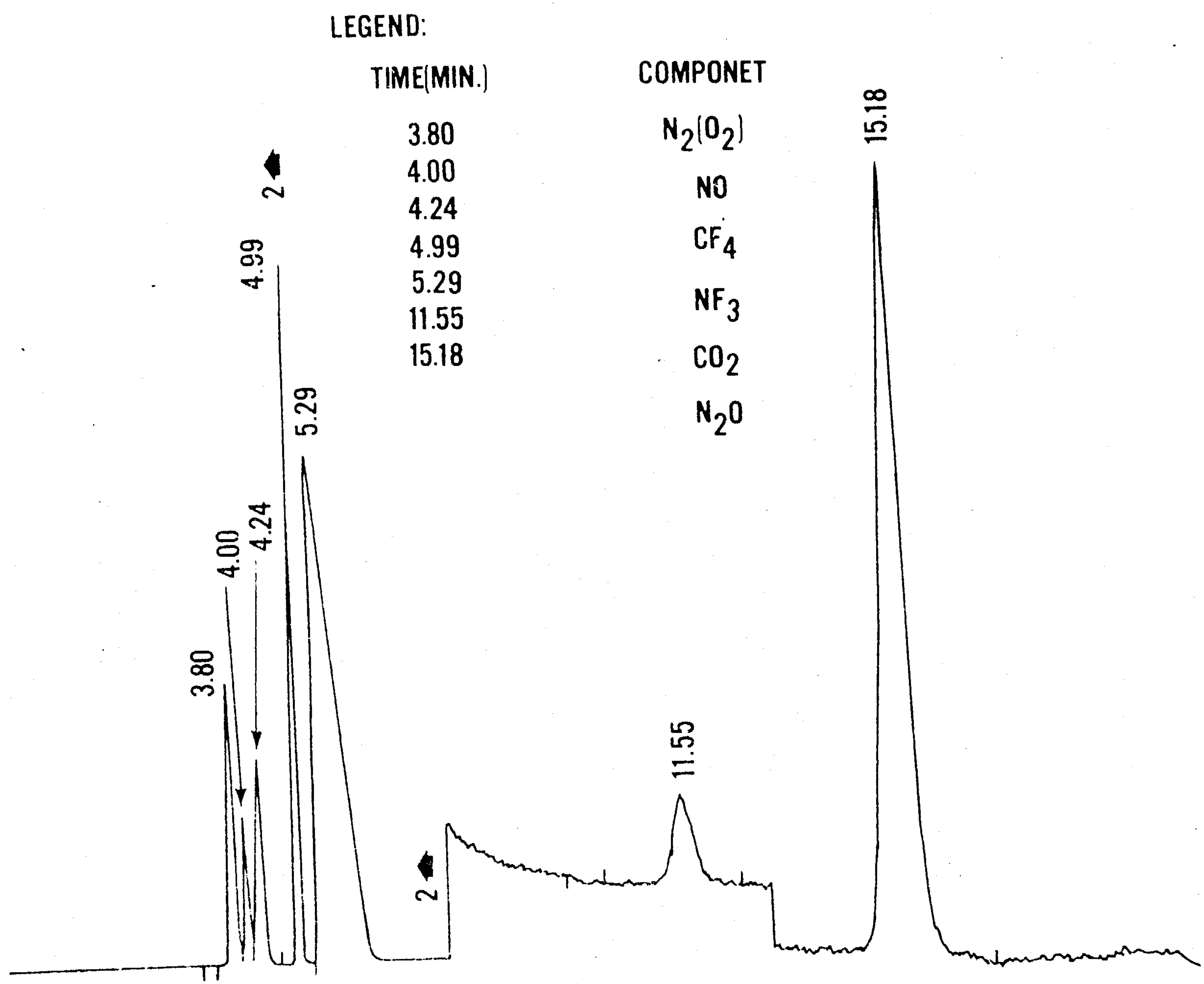


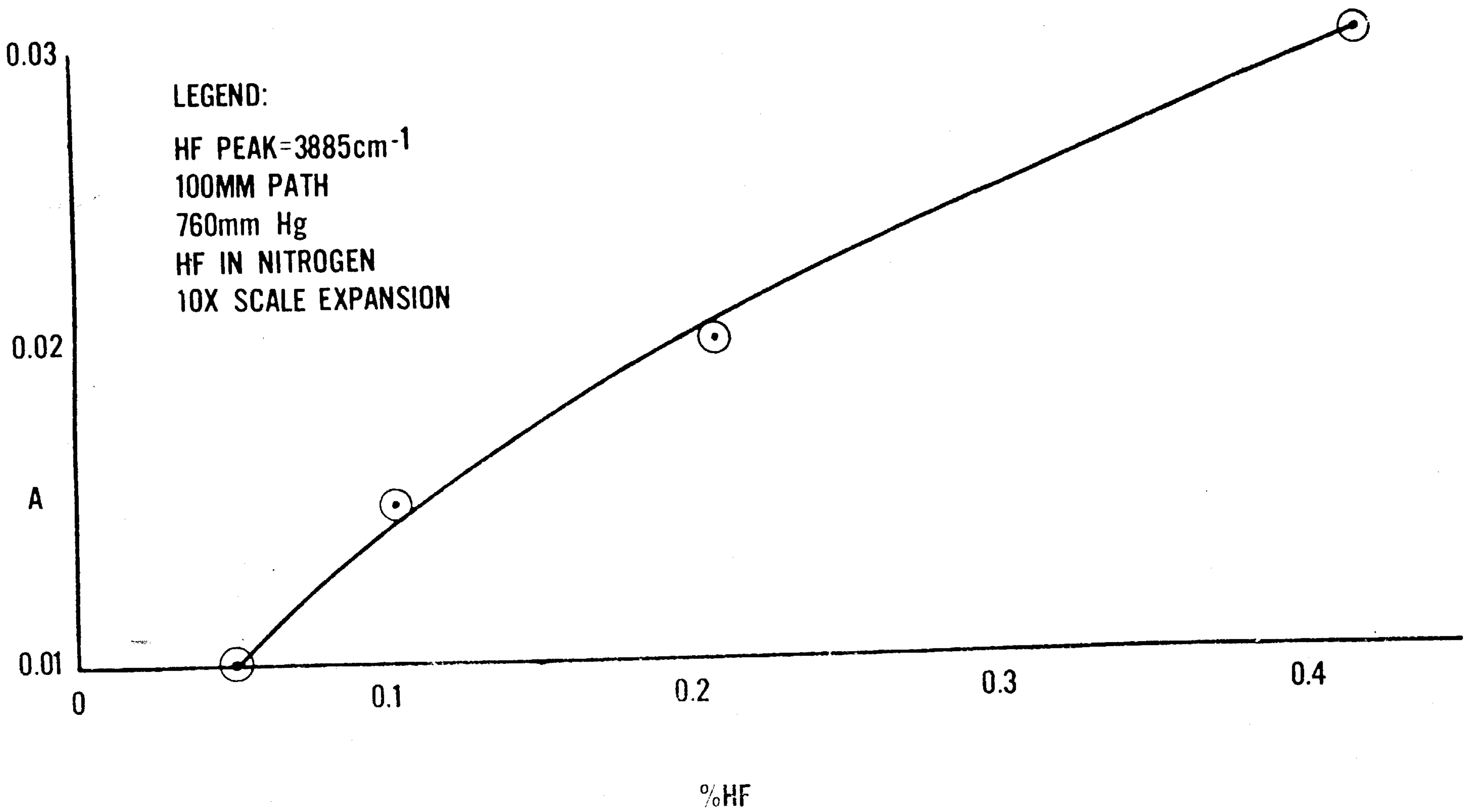
Table IV, NF_3 Analysis Results

Component	No Scrubber(%)	Scrubber(%)	Replicate range (6 determinations)
$N_2(O_2)$	0.23	0.21	0.04
CO	0.02	0.01	0.01
NO	0.02	0.02	0.00
CF_4	0.30	0.30	0.00
NF_3	99.35	99.39	0.05
CO_2	0.007	0.008	0.001
N_2O	0.08	0.08	0.00

Some minor differences are indicated, however, they are not significantly different from the replicate variation. If higher levels of oxidizing impurities were present in the NF_3 sample, use of the scrubber might affect the indicated levels of some measured impurities by release of similar reaction products (i.e., N_2 from N_2F_4 and N_2F_2, CO from COF_2, or NO from NOF). Thus, NF_3 which contains these reactive flourine compounds may be twice penalized for their presence.

Reactive fluoride analysis. Use of the infrared spectrophotometer for determination of HF in NF_3 is relatively common (1, 2, 6). Figure 7 is a typical calibration curve using data from standards prepared individually by partial pressure measurement in the 100 mm pathlength cell. It is apparent, from the low absorbance values, that scale expansion is useful at the noted test conditions. Other reactive fluorine compounds (ie., F_2, N_2F_4, NOF, N_2F_2, COF_2, etc.) have been determined by combinations of infrared spectrophotometry, red,/ox, titrimetry (1) and oxidation of Cl^- to Cl_2 with

Figure 7, HF ABSORBANCE VS. CONCENTRATION



subsequent gas chromatography analysis (2). These techniques are specific for total oxidizing species, however, their use necessitates several separate analyses and increased costs. If the primary reason for controlling these reactive species in NF_3 is to minimize corrosion then it seems a total reactive fluoride measurement would suffice.

Aqueous 0.1N-NaOH should hydrolyze the reactive fluorine compounds, leaving fluoride ion in proportion to the concentration and molecular formula of each specie. This will result in a graduated penalty for corrosion potential relative to the species present. This appears to be a desirable feature of the measurement.

The apparatus shown in Figure 2 was evaluated for collection efficiency with HF standards in nitrogen, NF_3, and HF in NF_3. Table V lists the data.

Table V, Evaluation of Total Active Fluoride Apparatus

Sample	%HF (calculated)	%HF (found)
HF/N_2	0.14	0.13
HF/N_2	0.19	0.19
HF/N_2	0.14	0.14
HF/N_2	0.12	0.15
HF/N_2	0.25	0.25
NF_3	-	0.004
NF_3*	-	0.000
HF/NF_3	0.21	0.22

*The NF_3 from the previous test was passed through a second bubbler

Using the test conditions described earlier, the final fluoride ion concentration is ~50ppm/wt. if the gas sample contains 0.1%HF. Table V data was obtained using sample flows through the bubbler of ~100 ml/min., thus indicating that the reaction is rapid and no losses are apparent.

CONCLUSION

A simple analysis technique for NF_3 has been demonstrated wherein a relatively complete quantitative description can be obtained with inexpensive laboratory equipment used with reasonable care.

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